Chapter 5

Acrylamide-*b*-*N*-isopropylacrylamide block copolymers: Synthesis by atomic transfer radical polymerization and effect of hydrophilic-hydrophobic ratio on solution properties

Abstract

A series of block copolymers of acrylamide and N-isopropylacrylamide (NIPAM) characterized by different ratios between the length of the two blocks have been prepared through atomic transfer radical polymerization in water at room temperature. The solution properties of the block copolymers were correlated to their chemical structure. The effect of the hydrophilic/hydrophobic balance on the critical micelle concentration (CMC) was investigated. The CMC increases at higher values for the solubility parameter, thus indicating a clear relationship between these two variables. In addition, the aqueous solution rheology of the block copolymers was studied to identify the effect of the chemical structure on the thermo-responsiveness of the solutions. An increase in the length of the NIPAM block leads to a more pronounced increase in the solution viscosity. This is discussed in the general frame of hydrophobic interactions strength. The prepared polymers are in principle suitable for applications in many fields, particularly enhanced oil recovery (EOR).

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5.1. Introduction

Acrylamide based polymers have been extensively studied and implemented in many different application fields such as, waste water treatment, cosmetics and oil recovery.[1, 2] Poly[*N*-isopropylacrylamide] (PNIPAM) and copolymers containing NIPAM have been extensively studied.[3] The unique property of PNIPAM in water, i.e. a transition from hydrophilic to partially hydrophobic character[4] with increasing temperature, can be utilized to prepare "smart" (responsive to external stimuli, in this case temperature) polymeric materials. Possible applications include among others, controlled drug delivery[5, 6] and gene therapy[7-9].

Controlled polymerization of NIPAM has been accomplished in water[10], different alcohols[11], and different mixtures of organic solvents and water[12-14]. Homopolymers of NIPAM will aggregate and form globules, which precipitate completely out of an aqueous solution if the temperature is increased above the lower critical solution temperature (LCST).[15] This can be a desired property in an application such as drug delivery. However, as temperature sensitive rheological modifiers, this is generally an undesired property since it leads to precipitation from the solution with consequent loss of any thickening effect. To mitigate this problem, a more hydrophilic monomer can be copolymerized with NIPAM.[3] At temperatures higher than the LCST of the NIPAM, the latter will induce association of copolymers chains while the hydrophilic segment of the copolymer will prevent (if it is long enough) the copolymer from precipitating out of the solution. According to this effect (i.e. the hydrophilic/hydrophobic balance), the incorporation of acrylamide, as the hydrophilic moiety, leads to an increase of the LCST, depending on the amount of acrylamide up to 100 °C.[16, 17] However, up to date the copolymerization of NIPAM with acrylamide has been reported through the use of free radical polymerization[16, 17] or coupling, i.e. grafting onto or grafting through, of separately prepared polyacrylamide and PNIPAM.[18, 19] Both synthetic pathways allow little, if any, control over the macromolecular structure and architecture, thus hindering the study of any reliable structure-property relationships.

In addition, given the hydrophobic character of NIPAM, when the polymer is dissolved in water a reduction of the surface tension is observed.[20] On the other hand, the incorporation of acrylamide, a more hydrophilic moiety, in the polymer dampens this effect.[16] The higher the fraction of acrylamide in the copolymer, the higher the surface tension of the corresponding water solution is (closer to the value measured when only pure PAM is used).[16] The combination of these properties (i.e. surface activity and rheology) renders these polymers very attractive at both academic and

industrial level. However, as anticipated (*vide supra*), these copolymers are usually synthesized by free radical polymerization and thus random copolymers, rather than block for which these effects are expected to be more relevant. In addition, the uncontrolled nature of the polymerization leads to a broad range of molecular weights and dispersities. These factors might hinder a deeper understanding of the relationship between the polymer structure and its solution properties. As a consequence and in order to widen the range of possible applications, it is crucial that the synthesis of the copolymers is controlled and that new synthetic strategies are developed for the synthesis of block-like structures.

The controlled polymerization of acrylamide has been published recently, both in an alcohol-water mixture[21] and, as reported recently by our group, in water[22]. In addition the synthesis of the block copolymer poly(acrylamide-*b*-*N*-isopropylacrylamide) in water was also accomplished.[22]

In this paper, the controlled synthesis of the block copolymers PAM-*b*-PNIPAM with varying length of the blocks is reported. First the PAM macroinitiators are prepared and subsequently NIPAM is polymerized on the macroinitiator as blocks (demonstrating the living character of the polymerization). To the best of our knowledge, this has not been accomplished before. The solution properties, i.e. CMC and solution viscosity as a function of shear rate and temperature, have been measured. Correlations between the chemical structure and the solution properties are provided. The solution properties are dependent on the hydrophilic-hydrophobic ratio of the copolymers. In addition, the surface properties of the block copolymers depend in a linear fashion on the solubility parameter.

5.2. Experimental section

Chemicals. Chemicals. Acrylamide (AM, electrophoresis grade, ≥99%), *N*-isopropylacrylamide (NIPAM, 97%), tris[2-(dimethylamino)ethyl]amine (Me_6TREN) copper(I) bromide (CuBr, 98%), copper(I) chloride (CuCl, 98%), glacial acetic acid, ethanol, diethyl ether and methyl 2-chloropropionate (MeClPr, 97%) were purchased from Sigma Aldrich. CuBr and CuCl were purified by stirring in glacial acetic acid for at least 5 hours, filtering, and washing with glacial acetic acid, ethanol and diethyl ether (in that order) and then dried at reduced pressure.[23] All the other chemicals were reagent grade and used without further purification.

PAM macroinitiator. The synthesis of the PAM macroinitiator was performed according to the literature method.[22] Detailed reaction conditions are summarized in Table 1. The volume of water used was kept constant at

1:6 (w:v) monomer to water ratio. The amount of catalyst used was 1:1.5 (mol:mol) initiator to CuCl and the same applied also for the ligand ratio (Me_6TREN). The reaction temperature was set at 25 °C and the reaction time was kept constant at one hour (except for the MI-530). The degree of polymerization (DP) of the macroinitiators was calculated by using the conversion (measured by GC) and the initial ratio between the monomer and initiator. The codes for the macroinitiators are defined as PAMX with X designating the number of AM units.

Block copolymerization, synthesis of PAM-*b*-PNIPAM. The macroinitiator PAM-Cl was synthesized according to the aforementioned procedure. An example of a block copolymerization is reported in the following. 0.5063 g (0.039 mmol) of the macroinitiator was added to a 100 mL round-bottomed flask along with NIPAM (2.1267 g, 18.8 mmol). Thirteen mL of demineralized water were added and the system stirred until the contents were dissolved. The mixture was degassed by three freeze–pump–thaw cycles followed by the addition of 5.8 mg (0.058 mmol) CuCl. The flask was placed in a thermostated oil bath at 25 °C. To start the reaction, 13.4 mg (0.058 mmol) Me_6TREN was added. All operations were carried out under nitrogen. After 60 minutes, the reaction was stopped by quenching with 87 mL of demineralized water (≈ 1/3 of the reaction volume or more if the reaction mixture is viscous). The contents were then purified via dialysis using membrane tubing Spectra/Por® Dialysis Membrane (molecular weight cut off [MWCO] = 2,000 g/mol). The product was then dried in an oven at 65 °C until constant weight and then grounded. The codes for the block-copolymers are defined as PAMX-*b*-PNIPAMY with X and Y designating the number of AM and NIPAM units respectively.

The degree of polymerization of NIPAM and the conversion of NIPAM is calculated using the following:

$$DPy = \frac{3 \cdot DPx}{\left(\frac{A_2}{A_1}\right) - 9} \tag{5.1}$$

$$Conversion\ \% = \frac{DPy}{\frac{[M]_0}{[I]_0}} \cdot 100 \tag{5.2}$$

DP_x is the number of monomeric units in the PAM macroinitiator and is obtained from Table 1. A_2 (protons of the polymer-backbone and of the methyl groups of the NIPAM units) and A_1 (proton on the first carbon next to the amide of the NIPAM unit) are the areas of the peaks defined in Figure 1. DP_y corresponds to the number of monomeric units in the PNIPAM that is

attached to the PAM macroinitiator. $[M]_0/[I]_0$ corresponds to the experimental initial monomer / initiator ratio.

Characterization. Acrylamide conversion was measured using Gas Chromatography (GC). One hundred µL of the sample taken from the acrylamide polymerization flask was dissolved in 17 mL of acetone (polymer precipitated) and injected on a Hewlett Packard 5890 GC with an Elite-Wax ETR column.

Proton Nuclear Magnetic Resonance (^{1}H NMR) spectra were recorded on a Varian Mercury Plus 400 MHz spectrometer using D_2O as the solvent. The NIPAM conversion was calculated by determining the ratio of the peak areas of AM units and the NIPAM units.

Surface tension was measured using the pendant drop method on a LAUDA DROP VOLUME TENSIOMETER TVT 1. A glass micro syringe was attached to a needle with a capillary radius of 1.055 mm. The temperature of the water bath was set to 25 °C and the density difference between air and water was set to 0.997 g/mL. Two sets of three measurements were taken and then averaged.

Viscosity measurements were performed on a HAAKE MARS molecular advanced rheometer. The software program used was the HAAKE Rheowin Job manager. The amount of sample used for each measurement was 2 mL. Solution viscosity was measured as a function of the shear rate (0.075 s^{-1} – 1750 s^{-1}, T= 20 °C) and as a function of temperature (shear rate 1.0 s^{-1}, T = 20 °C – 80 °C, 4 °C/min)

The cloud point of the different copolymers was determined by UV-Vis analysis. A Jasco V-630 UV-Vis spectrophotometer equipped with a temperature controlled six-position sample holder was used. The transmittance of the polymer solutions ([p] = 2 wt.%) was recorded at 500 nm at a heating rate of 0.2 °C/min from 20 to 70 °C against a reference sample containing demineralized water.

The hydrodynamic radius was measured through Dynamic Light Scattering (DLS). A Brookhaven ZetaPALS Zeta Potential Analyzer was used with a 659 nm solid-state laser. DLS was performed in dilute aqueous solution at 20 °C and a scattering angle of 90 °. In total 10 runs were performed for each sample (at equal polymer concentration, 0.0005 wt.%, i.e. below the CMC) and the mean and standard deviation are calculated for size distribution by weight assuming a lognormal distribution using the MAS OPTION software.

5.3. Results and discussion

5.3.1. Synthesis of the macroinitiators. The synthesis of the PAM macroinitiators was performed according to Scheme 5.1A and Table 5.1 using different molar ratios between the initiator and AM.

Scheme 5.1*: A, synthesis of the PAM macroinitiators (MI) and B, synthesis of the block copolymers PAM-b-PNIPAM*

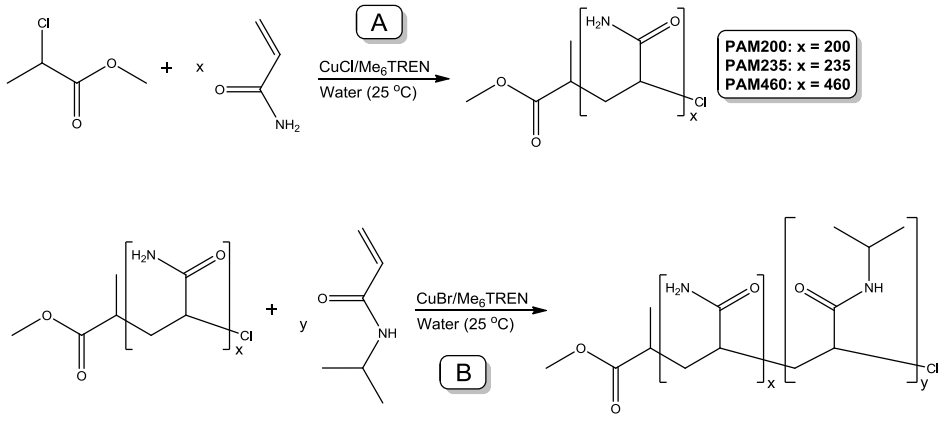

Table 5.1*: Synthesis of the PAM macroinitiators*

Entry	$[M]_0:[I]_0$	M/water (wt:vol); T; Time (min)[a]	Conv (%)	$M_{n,th}$[b] (g/mol)	DP
PAM200	300 : 1	1:6; 25 °C; 60	68	14 450	200
PAM235	300 : 1	1:6; 25 °C; 60	78	16 660	235
PAM460	680 : 1	1:6; 25 °C; 90	78	37 900	460

a: M = monomer, wt = weight, vol = volume in mL, T = temperature
b: Theoretical molecular weight = $[M]_0/[I]_0 \cdot conv.$

As can be observed in Table 5.1, three different macroinitiators were prepared with molecular weights varying between 14 000 to 38 000 g/mol. The controlled nature of the polymerization has been reported already.[22] Further evidence for the living/controlled character of the polymerization is provided by the ability to prepare block copolymers with NIPAM.

5.3.2. Synthesis of the block copolymers PAM-*b*-PNIPAM

The acrylamide macroinitiators synthesized in Table 5.1 were used as the initiators in the copolymerisation with NIPAM. A summary of the experimental conditions applied to synthesize the different copolymers is given in Table

5.2. Besides the monomer to initiator ratio, in one reaction also the scale of the preparation has been varied (important for further up-scaling).

***Table 5.2**: Synthesis of the different PAM-*b*-PNIPAM block copolymers*

Entry	$[M]_0:[I]_0$	M/water (wt:vol); T; Time (min)	Conv (%)[a]	$M_{n,\ ^1H\text{-}NMR}$	DP NIPAM	DP PAM	δ^b ($J^{1/2}\cdot cm^{-3/2}$)
PAM200-*b*-PNIPAM30	55 : 1	1:6; 25 °C; 60	57	17 600	30	200	27.8
PAM200-*b*-PNIPAM70	140 : 1	1:6; 25 °C; 60	50	22 150	70	200	26.5
PAM200-*b*-PNIPAM70	275 : 1	1:6; 25 °C; 60	26[c]	22 150	70	200	26.5
PAM200-*b*-PNIPAM90	140 : 1	1:6; 25 °C; 60	66	24 400	90	200	25.3
PAM200-*b*-PNIPAM155	270 : 1	1:6; 25 °C; 60	57	31 750	155	200	24.2
PAM200-*b*-PNIPAM185	550 : 1	1:6; 25 °C; 60	34	35 150	185	200	23.3
PAM200-*b*-PNIPAM650	1115 : 1	1:6; 25 °C; 60	59	87 750	650	200	22.7
PAM235-*b*-PNIPAM125	2495 : 1	1:6; 25 °C; 160	5	30 850	125	235	26.7
PAM460-b-PNIPAM10	750 : 1	1:6; 25 °C; 60	1	33 800	10	460	29.0

a: The conversion was determined by ^{1}H-NMR
b: Solubility parameter
c: The conversion is low, which might be due to the larger scale of the reaction

The largest block copolymer prepared was PAM200-*b*-PNIPAM650 and the smallest was PAM200-*b*-PNIPAM30. PAM460-*b*-PNIPAM80 was synthesized in order to have roughly the same total molecular weight as PAM235-*b*-PNIPAM125, even though it contains a different hydrophobic/hydrophilic ratio. These two polymers are compared (see below) to investigate whether the effects observed arise from an increase in molecular weight or from the increase in NIPAM content (i.e. hydrophobic/hydrophilic ratio).

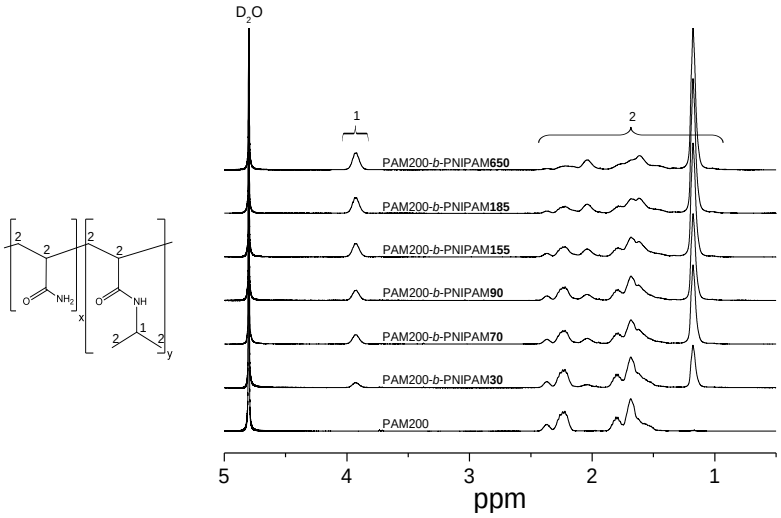

***Figure 5.1**: ^{1}H-NMR spectra of the block copolymers PAM200-b-PNIPAM(Y) and the parent macroinitiator*

As mentioned before, the conversions provided in Table 5.2 were determined using ^{1}H-NMR (Figure 5.1). The conversion can be calculated by comparing the ratio of the areas of resonances belonging to the protons of the first carbon of the isopropyl moieties of the polymer (labelled 1) and the ones for the rest of the protons labelled 2 (Figure 5.1). The ^{1}H-NMR spectra of the block copolymers (prepared with the macroinitiator PAM-200) are provided in Figure 5.1.

The resonance labelled as 1 (δ 3.9 ppm) represent the hydrogen atom of the CH group of the isopropyl group of PNIPAM and therefore the intensity of this resonance (in relation to the resonances labelled 2, δ 1.2 – 2.5 ppm) corresponds to the amount of PNIPAM polymerized on the PAM macroinitiator. The total area of the resonances labelled 2 correspond to the protons from the backbone of both the PAM and PNIPAM along with the 6 methyl protons of PNIPAM (2× CH_3). This area represents a total of 12 protons (9 from PNIPAM and 3 from PAM). Increasing the $[M]_0$:$[I]_0$ ratio leads to a higher area of the resonance corresponding to the NIPAM blocks indicating that longer NIPAM blocks are prepared (Figure 5.1). The ^{1}H-NMR spectra of the block copolymers agrees with the proposed structures.

5.3.3. Solution properties of poly(AM-*b*-NIPAM)

Solution viscosity as a function of shear. In Figure 5.2 the viscosity of the polymer solution (4 wt.% in demineralized water) as a function of the shear rate is displayed.

The polymers used are characterized by different hydrophilic (AM) / hydrophobic (NIPAM) ratios. All polymers consisted of a hydrophilic block of acrylamide (200 acrylamide units) and a hydrophobic block of PNIPAM of different lengths (and thus different total molecular weight).

At low shear rates a Newtonian plateau is observed, irrelevant of the length of the polymer or the number of NIPAM units. As the shear rate is increased (> 100 s^{-1}) shear thinning is observed (for PAM200-*b*-PNIPAM185 and PAM200-*b*-PNIPAM650), which is related to the disruption of the entanglements.[24] At higher shear rates ($\gamma \geq$ 500 s^{-1}) shear thickening is visible for the block copolymers containing PNIPAM block below 100 units. Given the low number of NIPAM units, the copolymer will behave more like polyacrylamide. Polyacrylamides are known to display shear thickening behaviour, related to structure formations (associations due to collision of chains arise[25]) and chain stretching, above a critical shear rate.[25, 26]

Figure 5.2 also shows that larger total molecular weights or larger NIPAM contents of the polymers result in higher starting viscosities of the solutions. It is unclear however from the results if this is due to the increase in

molecular weight or from the increase in the NIPAM content. As the NIPAM blocks increase in length so does the solution viscosity. The bulky isopropyl group of the NIPAM units inhibits the NIPAM blocks from coiling up as much as the AM units. Therefore as the NIPAM blocks increase in length the polymeric chain will be more extended. This leads to a higher hydrodynamic volume and thus a higher solution viscosity.

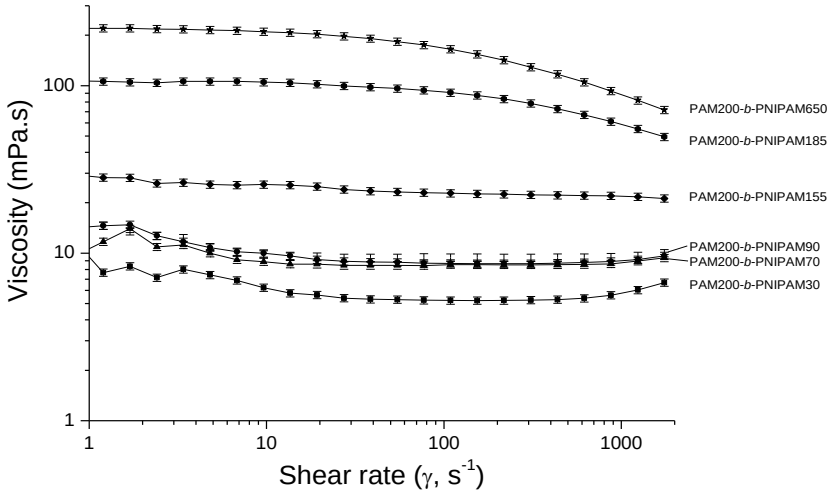

***Figure 5.2**: Viscosity vs shear rate of the PAMX-*b*-PNIPAMY series at a polymer concentration of 4 wt.%*

Four different polymers are compared (Figure 5.3) in order to elucidate which parameter, molecular weight or NIPAM content, has a more pronounced effect on the solution viscosity.

The PAM-PNIPAM ratio is different for three of the polymers used in the comparison; however the molecular weights are similar. A polyacrylamide of similar molecular weight (PAM460) is also included in the comparison. If the viscosity was solely dependent on the total molecular weight, then the solution viscosity of the four different solutions should be similar. However, as can be observed, clear differences can be distinguished. Although the $M_{n,tot}$ of PAM460 is larger than that of PAM235-*b*-PNIPAM125, it displays a lower solution viscosity. This confirms that the presence of NIPAM in the polymer has a much greater effect on the viscosity than the molecular weight. The comparison between PAM235-*b*-PNIPAM125 and PAM460-*b*-PNIPAM10 further justifies this conclusion, given the lower amount of NIPAM in the latter polymer. Further evidence for the increase in viscosity with increase in the NIPAM content can be obtained from the intrinsic viscosity

([η]).The intrinsic viscosity of the four different samples has been determined by taking the limit (c → 0) of the plots of the reduced viscosity as a function of the concentration (Figure 5.4).

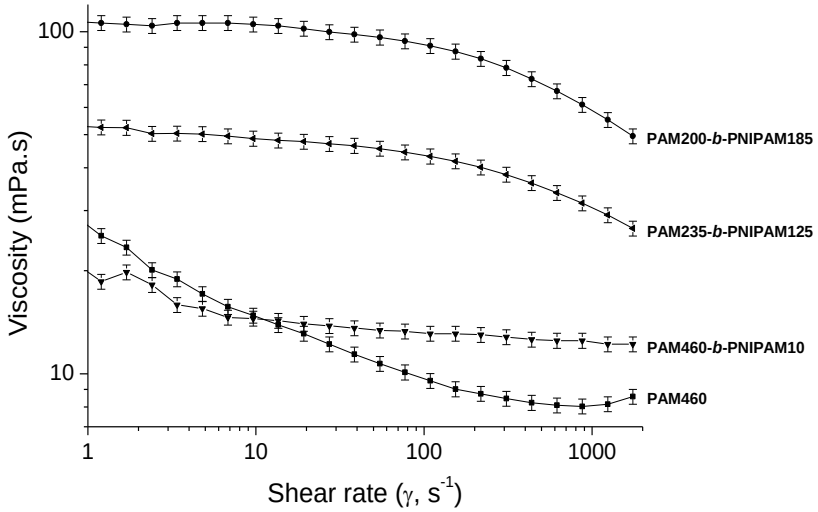

***Figure 5.3**: Solution viscosity vs shear rate for block copolymers of similar $M_{n,tot}$ but different PAM-PNIPAM ratios (polymer concentration is 4 wt.%)*

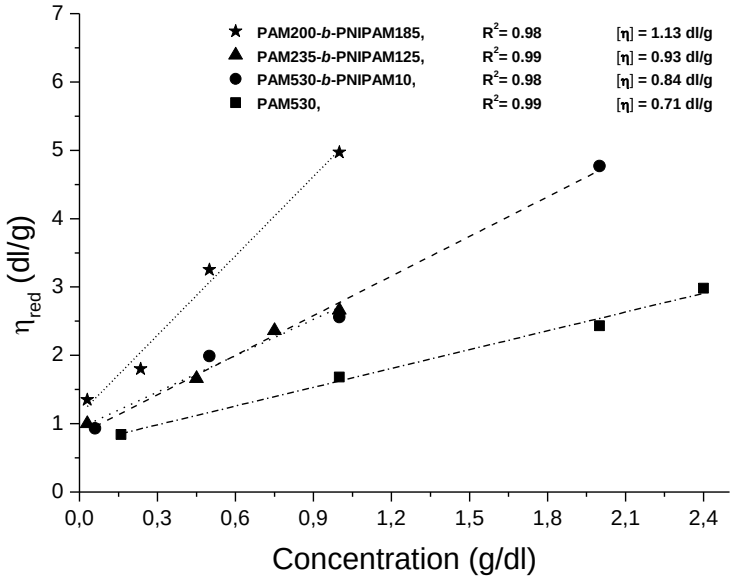

***Figure 5.4**: Reduced viscosity vs concentration for block copolymers of similar $M_{n,tot}$ but different PAM-PNIPAM ratios*

As evident in Figure 5.4, the $[\eta]$ increases with an increase in the NIPAM content of the copolymers. With these results it can be concluded that the differences observed in the solution properties of the four different samples (with similar $M_{n,tot}$ but different PAM / PNIPAM ratios) arise from the differences in the chemical structure.

The solution viscosity is also dependent on the hydrodynamic volume of the polymer chains in solution. DLS measurements demonstrate that the hydrodynamic volume is dependent on the hydrophobic-hydrophylic ratio (Table 5.3).

***Table 5.3**: Properties of the different block copolymers*

Entry	$R_{h,\ DLS}$ (nm)	$c^*_{equation\ 4}$ (wt.%)	5·c* (wt.%)
PAM530	57	0.0100	0.0500
PAM530-*b*-PNIPAM10	116	0.0010	0.0050
PAM235-*b*-PNIPAM125	99	0.0013	0.0065
PAM200-*b*-PNIPAM185	130	0.0006	0.0030

However, in order to evaluate what the effect is of the chemical structure on the rheological properties the comparison of the solution viscosities is performed at equal excluded volume (φ_s).[27] The concentration at which the polymeric chains start to overlap is defined as c^*, and can be calculated (equation 5.4) if the radius of gyration (R_g) or the hydrodynamic radius (R_h) is known.[28, 29]

$$\varphi_s = \frac{c}{c^*} = \frac{4 \cdot \pi \cdot R_g^3 \cdot N_{av}}{3 \cdot \rho \cdot M_w} \cdot c \tag{5.3}$$

$$c^* = \frac{M_w}{\frac{4}{3} \cdot \pi \cdot R_h^3 \cdot N_{av}} = \frac{M_w \cdot \rho^3}{\frac{4}{3} \pi \cdot R_g^3 \cdot N_{av}} \tag{5.4}$$

with N_{av} being the Avogadro constant, M_w is the molecular weight of the polymer, and ρ is the density of the solution. The comparison between the four different polymers is also done at a concentration of five times the critical overlap concentration ($5 \cdot c^*$) in order to have the same excluded volume, and the results are displayed in Figure 5.5.

The lower solution viscosity of the block copolymers at equal excluded volume demonstrates the effectiveness of hydrogen bonding to increase the solution viscosity. The solutions are well above the overlap concentration and

thus entanglements are present. The shear thinning behaviour observed (Figure 5.5) is related to the disentanglements of the chains and disruption of the weak hydrogen bonds. The hydrogen bonding capability of PAM is higher compared to PNIPAM. However, the hydrodynamic volume of a polymer chain increases (as evident from the R_h). Therefore the observed behaviour is a balance between the reduction in hydrogen bonding interactions and the increase in hydrodynamic volume. To conclude, the differences observed in the solution viscosities (Figure 5.3 and 5.5) of the different polymers arise due to the differences in chemical structure (PAM / PNIPAM ratio).

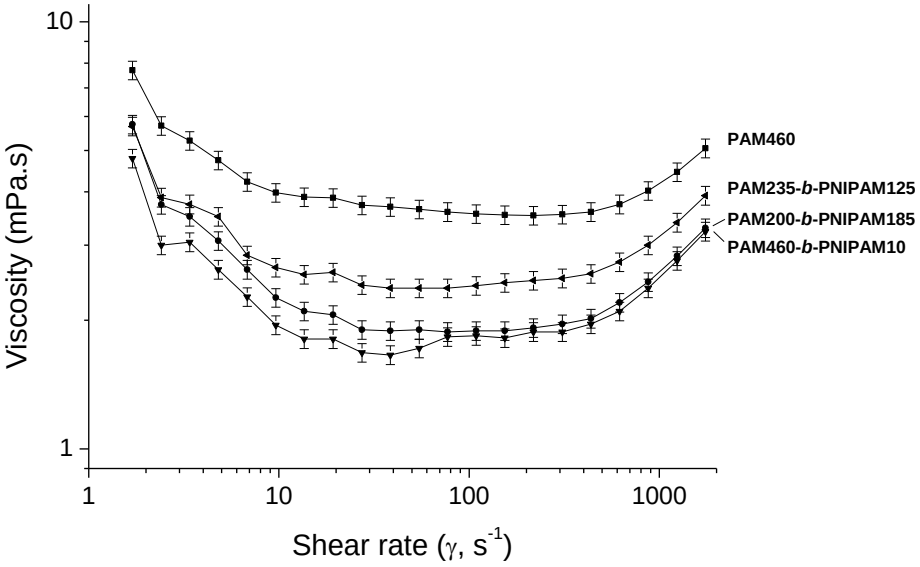

***Figure 5.5**: Solution viscosity vs shear rate for block copolymers of similar $M_{n,tot}$ but different PAM-PNIPAM ratios at the same excluded volume (polymer concentration is $5 \cdot c^*$)*

To the best of our knowledge this constitutes a novel insight into the effect of different structural parameters (such as hydrophobic/hydrophilic balance and molecular weight) on the corresponding solution viscosity. Indeed, to date, a systematic study of the roles that molecular weight, hydrophobic group content and distribution (within the copolymer sample) play in solution properties has not yet been reported.[30]

Solution viscosity as a function of temperature. The viscosity was measured as a function of the temperature of the solution and the results are displayed in Figure 5.6. The polymer concentration of the solutions was set at 2 wt. %. All polymers consisted of a hydrophilic block of acrylamide (roughly

14 000 g/mol or 200 acrylamide units) and a hydrophobic block of PNIPAM of differing length, resulting in polymers with different total molecular weights. The shear rate during the temperature sweep was fixed at a value of 1.0 s^{-1}. To illustrate the effect of NIPAM on the behaviour of the block-copolymers in solution as a function of temperature, the homopolymer PAM460 is also displayed in Figure 5.6. As can be observed in Figure 5.6, a clear peak in the viscosity near 32 °C can be distinguished, except for the homopolymer (PAM460).

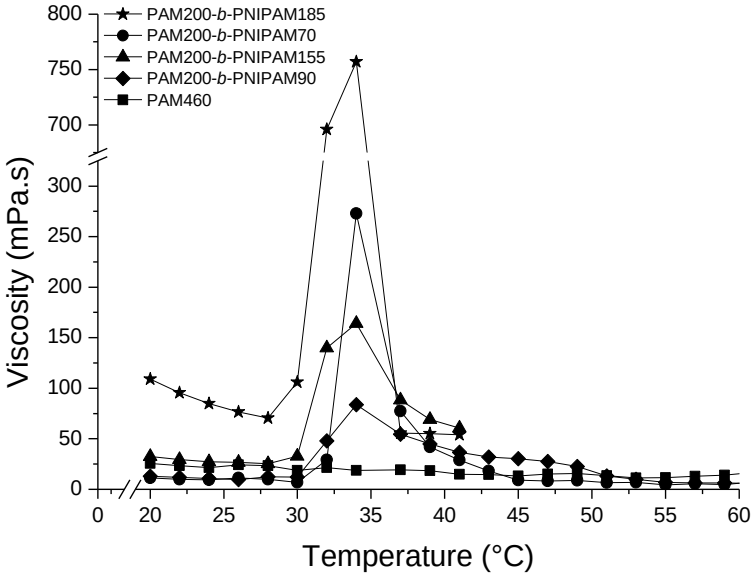

***Figure 5.6**: Solution viscosity of 4 wt. % polymers solutions vs temperature*

The temperature at which an increase in viscosity is observed does not change with the NIPAM content, and corresponds to the LCST of PNIPAM. As the temperature increases from 20°C the viscosity slowly decreases before it significantly increases to a peak near 32 °C. After the peak, the viscosity decreases rapidly as the temperatures further increases, stabilizing near the initial viscosities measured before the peak. The same behaviour in the solution viscosity at temperatures below and near the LCST is also observed for the homopolymer of *N*-isopropylacrylamide.[31-33] When the temperature of the polymer solution reaches the LCST, the isopropyl groups of the PNIPAM blocks are dehydrated and aggregation between the PNIPAM blocks arises.[33] The increase in viscosity in that region indicated that some of this association is intermolecular leading to the observed increase in solution viscosity. The decrease in viscosity above the LCST is a result of the majority of the chains

precipitating into macromolecular aggregates[31, 33] and the decreased viscosity of the solvent. However the peaks displayed in Figure 5.5 signify a response of the polymer to changes in temperature. When comparing PNIPAM to anionic polyacrylamide (HPAM), which has a similar structure[32], the HPAM follows the well-known trend of decreasing viscosity as a function of temperature. Therefore the peak exhibited for the PAM-*b*-PNIPAM block copolymers is attributed solely to the presence of NIPAM moieties.

Looking more closely to the peaks it is clear that decreasing the NIPAM content (from 185 to 155 units) resulted in a decrease in the peak viscosity from above 700 mPa.s to 275 mPa.s respectively. The peak viscosity reduces further with smaller blocks PNIPAM. The smaller the PNIPAM blocks are, weaker hydrophobic aggregations arise. In general, the significant increase in the solution viscosity for hydrophobically associating polymers results from the intermolecular aggregation between the hydrophobic groups.[1] The aggregation results in larger hydrodynamic volumes, which in turn, increase the viscosity of the solution. By increasing the shear rate, these intermolecular associations are disrupted resulting in the decrease of the hydrodynamic volume and therefore the solution viscosity.[1]

Critical micelle concentration (CMC). The critical micelle concentrations were measured by plotting the surface tension (against air) of a polymer at different concentrations (Figure 5.7).

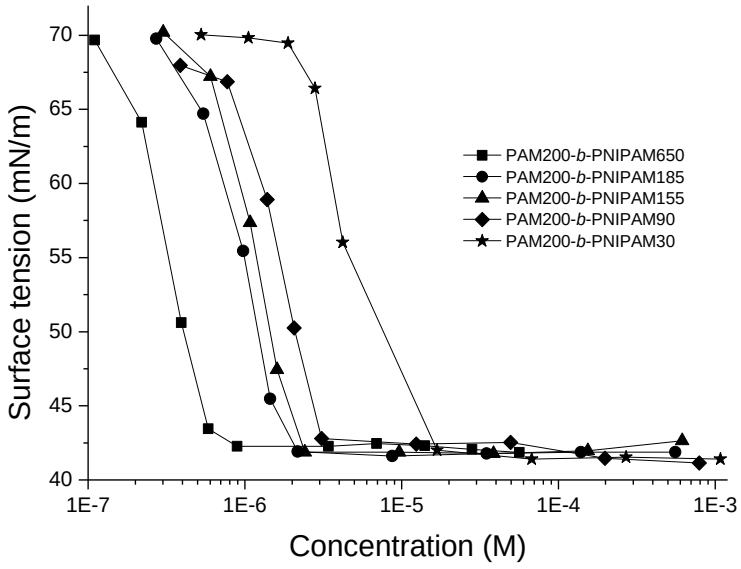

***Figure 5.7**: Surface tension against the polymer concentration of 5 different copolymers*

As can be observed in Figure 5.7, S-shaped curves are obtained, which correspond to those expected.[34] For low polymer concentrations the solutions move towards the surface tension of demineralized water (measured to be 70.47 mN/m). As the concentration increases, the surface tension reaches a region where it decreases dramatically. Then at a specific concentration, the surface tension stops decreasing with a minimum value near 41.5 mN/m. This specific concentration is known as the critical micelle concentration (CMC). Remarkably, all the samples display a surface tension close to the value of pure PNIPAM, albeit with different CMCs (as will become evident later). This is in stark contrast to random copolymers of AM and NIPAM, where the final surface tension is a function of the composition of the copolymer.[16] The surface tension for a 50-50 (mol ratio) random copolymer is 51.0 mN/m, compared to 41.5 mN/m for PAM200-*b*-PNIPAM185.

Graphically the CMC can be obtained from the plot in Figure 5.6 by taking the line of best fit in two places and noting the concentration at the intersection[35] (not shown for brevity). As the PNIPAM block length increases the concentration needed for micelle formation decreases. This is expected as the larger the PNIPAM blocks are, the larger the effect of its lower hydrophilicity.[16] The order of magnitudes 10^{-6} and 10^{-7} M coincide with that given in literature for amphiphilic block copolymers.[36] The formation of micelles is a result of the concentration of polymer being high enough such that interaction between the PNIPAM blocks is beneficial. The aggregation of less hydrophilic blocks result in the formation of a micelle with a hydrophobic core (PNIPAM) and a hydrophilic corona (PAM) keeping the micelles stable in the water solution.[36]

To justify the correlation between the CMC and the PNIPAM content, the solubility parameter (δ) was plotted as a function of the CMC (Figure 5.8). The solubility parameter was calculated using a group contribution theory[37], which takes into account the structure of the polymer and the molar % of each block. This is similar to the hydrophilic-lipophilic balance (HLB), which calculates the balance based on molecular weight percentage of each block. For an acrylamide homopolymer the solubility parameter is 29.14 $J^{1/2}\cdot cm^{-3/2}$. For a pure PNIPAM polymer the solubility parameter is 22.07 $J^{1/2}\cdot cm^{-3/2}$. Therefore the copolymers should have decreasing solubility parameters as the PNIPAM block increase in length.

As shown by Figure 5.8 the CMC increases linearly as a function of the solubility parameter. This confirms the general trend for non-ionic surfactants[38] where the CMC increases as the hydrophilic content increases. In literature, however the hydrophilic/hydrophobic balances are depicted by the HLB number and not the solubility parameter.[36] The solubility parameter

takes into account the structure of the each block and their molar ratios and the HLB number only looks at the molecular mass ratio of each block. As a result, comparing the solubility parameter with the CMC illustrates a structure-property relationship for the CMC and surface activity. This enables the design of block copolymers with predictable surface properties and renders the laborious measurements obsolete.

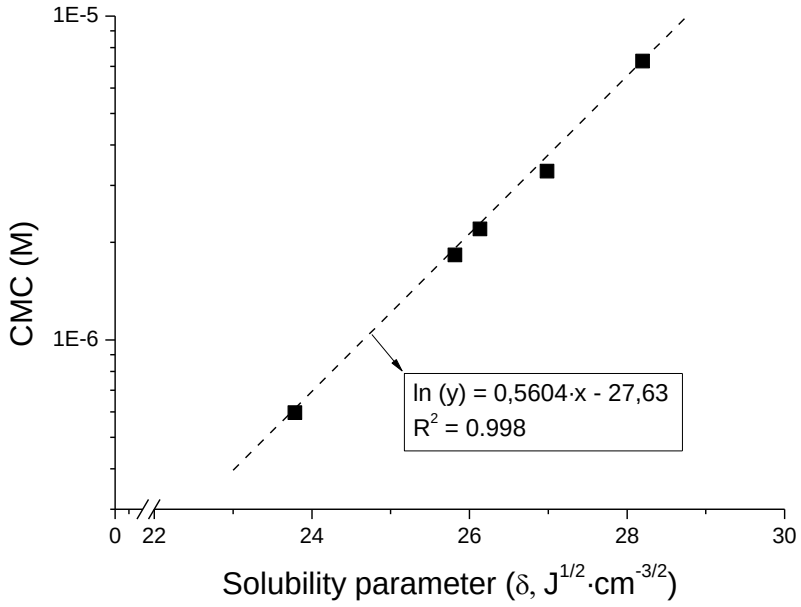

***Figure 5.8**: The solubility parameters vs. the CMC*

Effect of the chemical structure on the cloud point. The cloud point of four different block copolymers was determined with UV-Vis (Figure 5.9). The comparison of the different block copolymers demonstrates that by decreasing the length of the NIPAM block an increase in the cloud point can be obtained. Similar results were obtained for random copolymers of AM and NIPAM.[16] Random copolymers of AM and NIPAM of higher molecular weights display cloud points that are dependent on the ratio between the two moieties.[39]

A decrease in the NIPAM content from 85 to 55 mol% leads to an increase in the cloud point from 42 to 74 °C.[39] As can be observed in Figure 5.8, a decrease in the NIPAM content from 48 to 13 mol% leads to a slight increase in the cloud point from 32 to 34 °C. Copolymers of NIPAM and AM with 50 mol% of AM[16] (or 40 mol%[39]) display a cloud point above 100 °C. Of all the samples tested (AM content varies between 52 and 87 mol%), the

cloud points were all below 35 °C. This significant difference (compared to the literature) is attributed to the fact that the NIPAM units in the block copolymers can form a globule more readily compared to that of a random copolymer. Therefore, the block copolymers can precipitate out of the solution much easier compared to random copolymers.

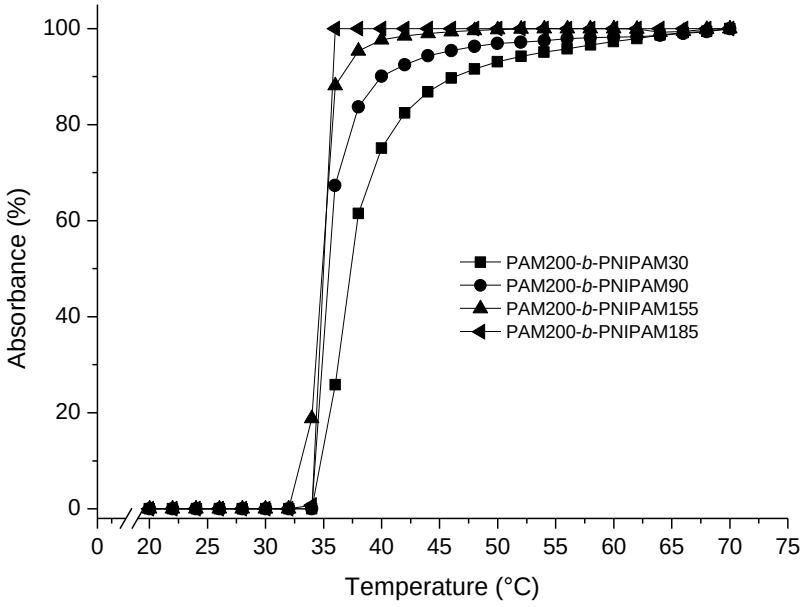

***Figure 5.9**: LCST determination by UV-Vis light transmittance ([p] = 2 wt.%)*

5.4 Conclusion

Block copolymers of AM and NIPAM have been prepared by ATRP in water at room temperature. The controlled nature of the polymerization allowed for the synthesis of block copolymers with varying block lengths of both monomers. The aqueous solution properties of the block copolymers were correlated to their chemical structure. The effect of the hydrophobic-hydrophilic ratio on the LCST, CMC, and solution rheology was investigated. A clear correlation exists between the solubility parameter and the CMC, the latter decreasing with the former. The LCST of the block copolymers is dependent on the balance between the two moieties. The longer the NIPAM block length, the closer the LCST is to the one of the NIPAM homopolymer. The solution viscosity is also dependent on the chemical structure. Longer

blocks of NIPAM lead to a higher solution viscosity, which is related to the more extended nature of the NIPAM blocks (compared to AM ones).

The correlation between the solubility parameters and the surface properties of the copolymers offers the possibility of predicting the surface properties of block copolymers without the need to measure them. These new insights, coupled with the novelty of the synthetic strategy pave the way for application of these materials in e.g. EOR, drug delivery and cosmetics.

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